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EFFECTS OF BORON DOPING ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CADMIUM OXIDE THIN FILMS PREPARED BY SOL-GEL SPIN COATING METHOD

M. Thirumoorthi

Assistant Professor of Physics, H. H. The Rajah's College, Pudukkottai.

Dr. J. Thomas Joseph Prakash

Assistant Professor of Physics, Government Arts College, Tiruchirappalli.

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ABSTRACT

Undoped and boron (B) doped cadmium oxide (CdO) thin films were obtained using cadmium acetate dehydrate and boric acid as precursor solutions by sol-gel spin coating method. The films were annealed at 500 oC and structural, electrical, optical and surface properties have been investigated. The recorded X- ray diffraction patterns indicated that all the films had preferential orientation along (111) plane and fit well with the cubic crystal structure. The minimum resistivity of 1.71×10-3 Ω cm was obtained for the film doped with 2.5 wt% boron. Scanning electron microscopy (SEM) images indicates that the boron doping was strongly influenced on surface morphology. An EDX spectrum shows that Cd and O elements are present in the solid films. Optical spectra showed that the average transmittance of doped films over 80 % in the visible region and the obtained optical band gap is higher (2.56 – 2.59eV) than the undoped (2.23eV) cadmium oxide thin films.

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INTRODUCTION

In recent years, transparent conducting oxides (TCO) from a II-VI group of semiconductors have received much attention on their wide applications in the field of optoelectronic devices due to its unique properties of high transparency and low resistivity [Seval Aksoy 2009, Ananthi.R 2012]. The cadmium oxide (CdO) thin film has a low energy band gap (2.2eV to 2.47eV) and higher mobility values, which are necessary for high conductivity TCO materials [Seval Aksoy 2009]. Various types of techniques such as spray pyrolysis [Lokhande.B.J, 2004], metal organic chemical vapor deposition [Lamb.D.A, 2011],

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chemical bath deposition [De.L.R, 2006], RF magnetron sputtering [Saha.B, 2007], pulsed laser deposition [Gupta.R.K, 2008], successive ionic layer adsorption and reaction [Salunkhe.R.R, 2009], Sol-gel process [Seval Aksoy 2009, Abdolahzadeh.A, 2011] have been employed to prepare CdO thin films. Among these, the sol-gel process has several advantages such as composition control, homogeneity, purity and simplicity over the other techniques. The doping of group III elements (such as Al, Ga, In, B) with cadmium oxide exhibits better crystallinity and electrical conductivity. There are several reports on doping of Aluminium [Murali.K.R, 2010], Gallium [Deokate.R.K, 2010], Tin [Zheng.B.J. 2011], Indium [Gupta.R.K, 2008] and Boron [Yakuphanoglu.F, 2011] with Cadmium oxide thin film. The electrical conductivity, mobility and optical band gap of CdO thin films can be controlled by doping of boron [,Yakuphanoglu.F, 2011, Lokhande.B.J, 2013]. In the present work boron doped cadmium oxide (CdO:B) thin films were prepared by sol-gel spin coating method. The structural, electrical, optical and surface properties were studied as a function of different doping concentrations.

EXPERIMENTAL PROCEDURE

We have synthesized cadmium oxide thin films on glass substrate by sol-gel spin coating method. Taking the starting materials cadmium acetate dehydrate (Loba-99.9%) and Boric acid (Merck-99.9%). First 0.2 M of cadmium acetate dehydrate was dissolved in a mixture of 80ml 2-methoxyethanol and 20 ml of ethanol. The mixture was stirred at 70 ^{o}C for 2 hours and then it was allowed to cool room temperature for 30 min under continues stirring. For boron doped cadmium oxide solution, a similar procedure was done. The boron concentrations in the solution maintained at 0, 2.5, 5, 7.5, 10 wt% with respect to cadmium concentration. Before coating the glass substrate was cleaned using chromic acid, deionized water and acetone by stepwise. The coating solution dropped into the glass substrate (1×1 inch), which was rotated at 2000 rpm for 30sec using spin coater. After coating, the film was dried at 100 ^{o}C for 10 min to evaporate the solvent and remove the organic residuals. The above procedures were repeated three times to obtain film with sufficient thickness. Thereafter the films were annealed at different temperature of 200, 300, 400, 500 ^{o}C in furnace for 1 hour.

The thickness of the film was measured by profilometer (SJ-301 Mitutoyo). The structural property of the films was evaluated using X-ray diffractometer (X'pert PRO PANalytical) with Cu kα_1 radiation λ=1.54056 Å. Surface morphology was studied using scanning electron microscope (ESEM QUANTA200, FEI-Netherland). Optical transmittance and absorbance recorded with UV-Vis spectrophotometer (Oceans optics HR2000-USA) in the range 300 – 1200 nm. The electrical resistivity of the film was measured at room temperature using four point probe method.

RESULTS AND DISCUSSIONS

3.1 Structural Properties

The crystal structure of sol-gel derived CdO:B thin films were identified by X-ray diffraction. Fig.1 and Fig.2 shows the XRD patterns of CdO:B thin films prepared at different annealing temperature and different doping concentration respectively. The diffraction peaks observed in the XRD patterns of all the films corresponds to (111), (200) and (220) planes of the typical cubic crystal structure of CdO thin films compared with JCPDS CARD: 75-0592. The patterns of films for different annealing temperature shows as the crystallized temperature increased the intensity of the (111) diffraction peak increased, which indicates that crystallization quality was improved. Similar behavior is reported earlier by several reporters [Bilgin.V, 2010, Santos-Cruz.J, 2005]. Film annealed at 200 °C did not exhibit any significant peak and were therefore deemed amorphous. This result reveals that 500 °C is optimized temperature for CdO:B thin films. The XRD pattern of different doping concentration shows that the preferential orientation is along the (111) plane for all the films. The intensities of the diffraction peak of (111) plane tended to slightly decreased with increasing boron concentrations.

The average grain size of the CdO:B films was calculated for prominent peak (111) using the Sherrer's formula

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Table – 1: *Structural Parameters of Undoped and Boron Doped Cadmium Oxide Thin Films*

Samples	Preferential Orientation	d-spacing (Å)	Grain Size (D) (nm)	Dislocation density (δ) ×10^{14} (lines/m^2)	Lattice constant (Å)
Undoped	(111) CdO	2.71031	87.45	1.3076	4.6943
2.5wt% B	(111) CdO	2.70759	40.24	6.1756	4.6896
5wt% B	(111) CdO	2.70528	39.54	6.3962	4.6856
7.5wt% B	(111) CdO	2.71024	35.66	7.8638	4.6942
10wt% B	(111) CdO	2.71193	34.27	8.5147	4.6972
JCPDS card 75-0592	(111) CdO	2.71050	-	-	4.6940

Figure – 1: *X-Ray Diffraction Spectra of CdO:B Thin Films Annealed at Different Temperature.*

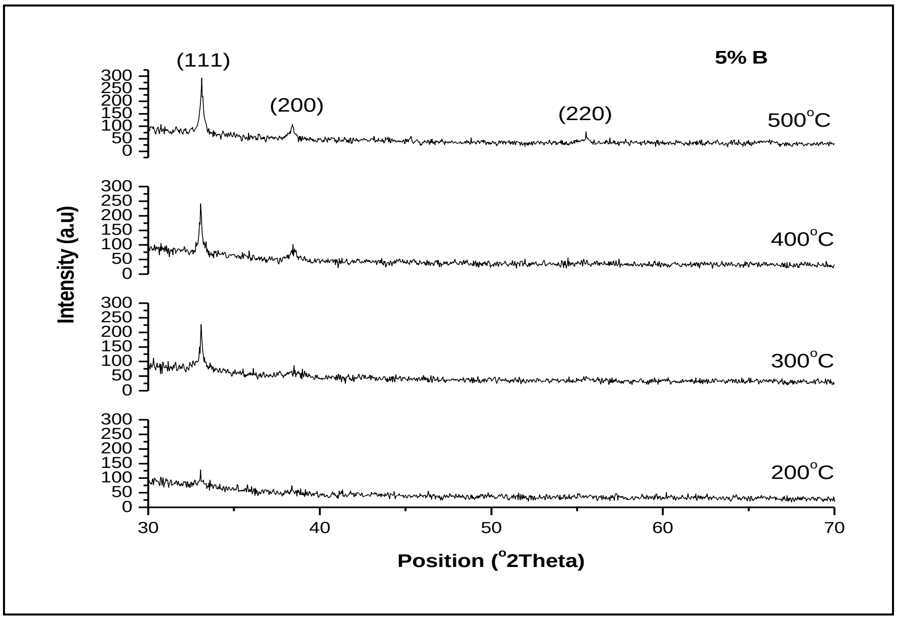
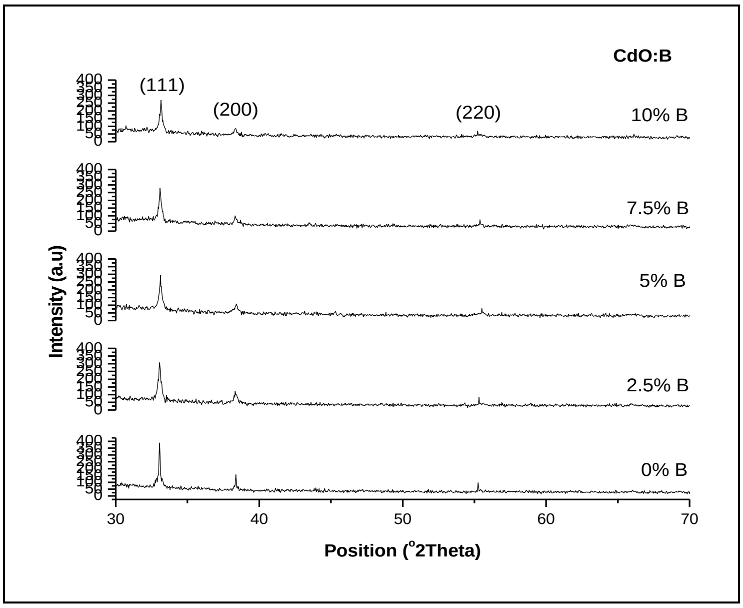


Figure – 2: *X-Ray Diffraction Spectra of CdO:B Thin Films for Different Doping Concentrations*



Where λ (1.54060 Å) is the wavelength of incident X-ray of Cu kα$_1$ line, 'β' is the full width at half maximum (FWHM) measured in radian and 'θ' is the Bragg's angle of the diffraction peak (111). The lattice constant (a) for cubic structure and the dislocation density (δ) are calculated by following relations,

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

$$\delta = \frac{1}{D^2}$$

Obtained values are tabulated in Table 1. When increasing boron doping the grain size was decreased as decreased the intensity of the diffraction peak (111). The calculated lattice constant and the d-spacing values of pure and 7.5 wt% boron doped cadmium oxide thin films agree well with standard values (JCPDS card : 75-0592). The dislocation density is measured the defects in the crystal structure and the minimum value is obtained for undoped films.

3.2. Surface Morphology and Elemental Analysis

It is known that the surface property of the transparent conducting oxide films influences their optical and electrical properties which are important factors for applications of optoelectronic devices. Fig.3 shows the surface morphology of CdO:B thin films deposited as a function of boron concentration on glass substrate at 30000x magnification of all samples. It shows surface of all the samples exhibit uniform distribution of particles. The pure CdO film shows bud shaped large grains and all the boron doped films exhibit spherical shaped grains. The results reveal that increasing boron concentration the grain sizes and voids were decreased, which agreed with the XRD result.

The elemental analysis of the films was confirmed by energy dispersive X-ray spectroscopy (EDX). The EDX spectra of boron doped cadmium oxide thin films are shown in Fig.4. The spectrum shows that the Cd, B and O elements in the starting solution present in the solid film. However, the amount of cadmium increases and oxide decreases with increasing boron incorporation.

3.3. Optical Properties

The optical transmittance spectra of CdO:B thin films for different doping concentrations is shown Fig.5. It can be seen that the transmittance of the undoped CdO film is very low. Similar results have been reported previously for CdO thin films by Salih et al [Salih Kose,2009]. All the boron doped films show average transmittance in the range of 72 % to 87 %.

Figure – 3: *Scanning Electron Micrograph (SEM) Images of Boron Doped CdO Thin Films*

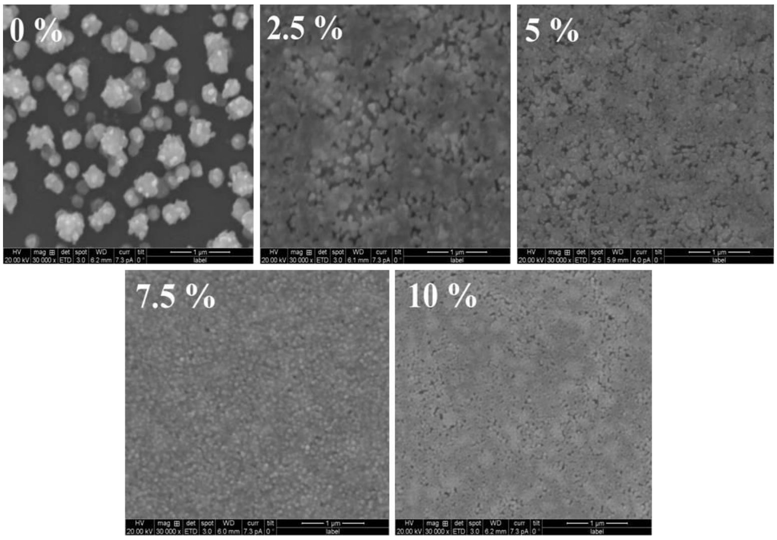
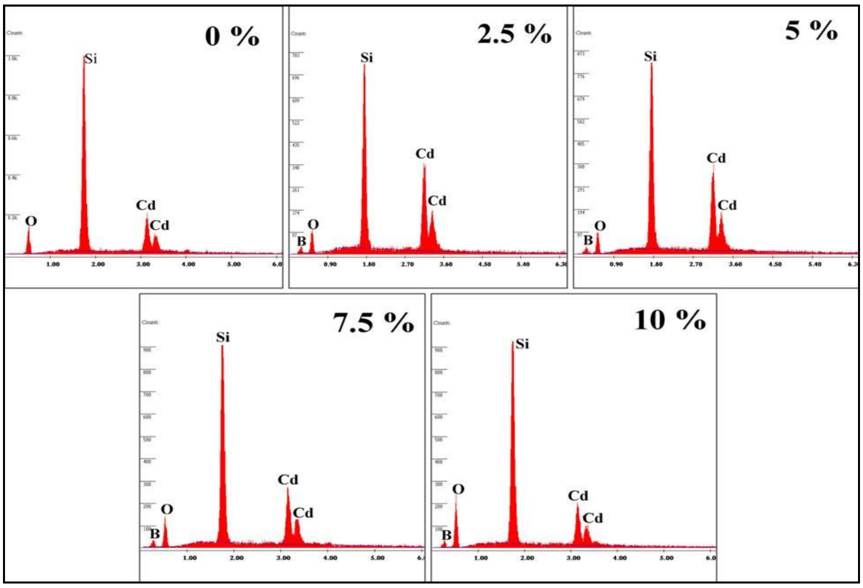


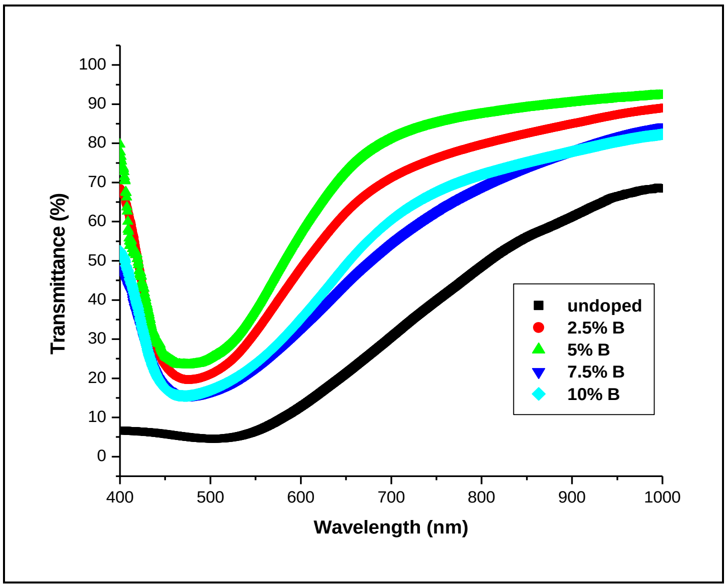
Figure – 14: *EDX Spectra of Boron Doped CdO Thin Films*



The effect of boron doping on the transmittance of CdO films may be due to the surface effects. For 2.5 wt% and 5 wt% of boron doping had the average transmittance is 82 % and 87 % respectively, which meets the required transmittance of transparent conducting oxides (TCO) thin film applications. For 7.5 wt% and 10 wt% the average transmittance is 72 % and 73 % respectively, which suggest that more doping decreases the transparency due to increased absorption by free carriers [Wu.X, 1997].

The optical band gap (E_g) of the CdO:B thin films were determined by extrapolation of the linear portion of $(\alpha h\nu)^2$ .vs. hν plots using the standard relation,
$(\alpha h\nu)^2 = B\,(h\nu - E_g)$

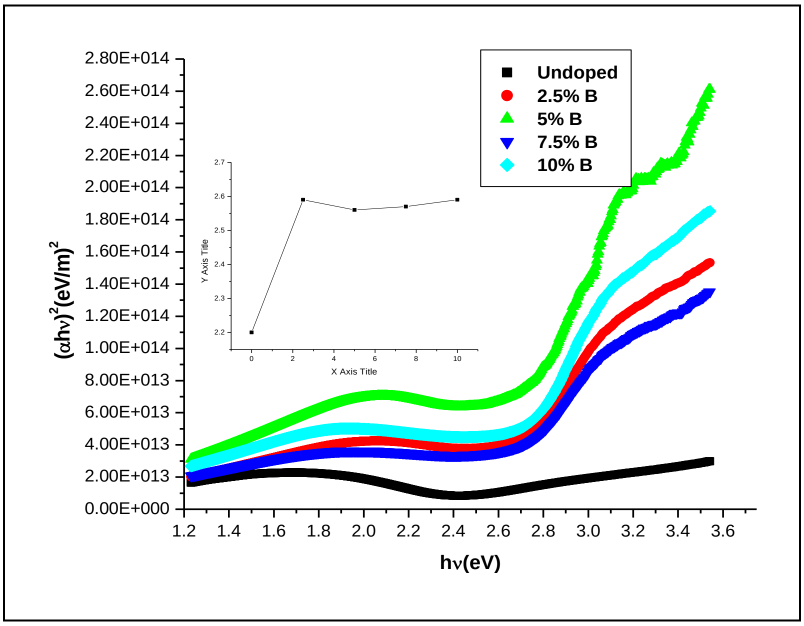
Figure – 5: *Optical Transmittance Spectra for Undoped and Boron Doped CdO Thin Films*



Where 'α' is the absorption coefficient, 'hν' is photon energy, 'E_g' the optical band gap energy and 'B' is the constant depending on the electron-hole mobility. The absorption coefficient (α) is expressed as,

$$\alpha = \frac{1}{d}\ln(1/T)$$

Figure – 6: *The $(ah\nu)^2$ Versus Photon Energy (hν) for Undoped and Boron Doped CdO Films*

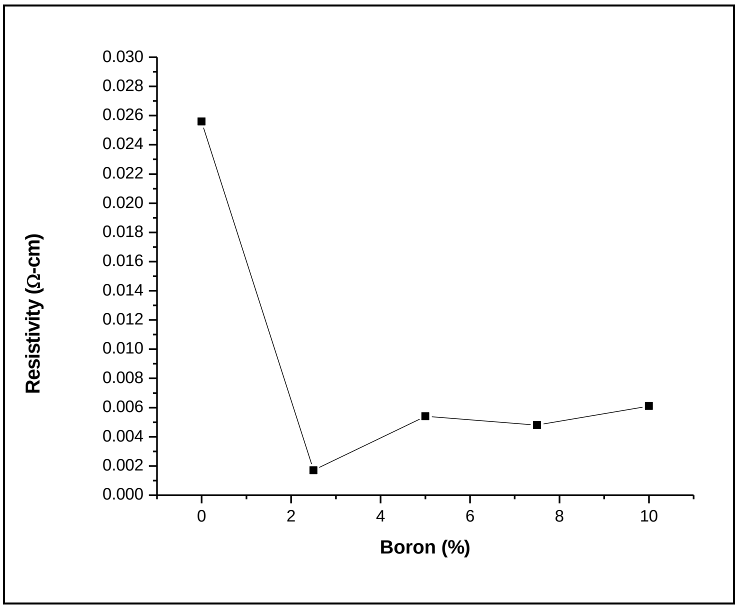


Where T is transmittance (%) and d is film thickness. Obtained band gap values are plotted (in set) as a function of boron concentration is shown in Fig.6. This indicates that the optical band gap of CdO films can be controlled by boron doping. For undoped CdO thin film obtained value is 2.23eV. Previously the similar band gap values have been reported for the CdO films deposited by sol-gel method as 2.22eV [Seval Aksoy, 2009], 2.23eV [Abdolahzadeh.A, 2011] and 2.27eV [Yakuphanoglu.F, 2011]. The obtained band gap values for 2.5, 5, 7.5 and 10 wt % of boron doping is 2.59, 2.56, 2.57 and 2.59eV respectively, which are higher values than earlier reported values for CdO:B by sol-gel dip coating method [Yakuphanoglu.F, 2011]. The blue shift of band gap is related to the Burstain – Moss effect.

3.4. Electrical Properties

The measured electrical resistivity of CdO:B thin films as a function of boron concentration is shown in Fig.7. It can be seen that the electrical resistivity of all the boron doped films is lower than undoped cadmium oxide (2.5610^{-2} Ω cm) thin film. It is revealed that the carrier concentration is increased when boron doping. The 2.5 wt% boron doped CdO thin films exhibit the lowest resistivity (1.76×10^{-3} Ω cm) among all the doped films, which is lower than the reported value for CdO:B by sol-gel method [Yakuphanoglu.F, 2011]. After 2.5 wt% of boron doping the resistivity was increased slightly, which caused may be due to lower crystal orientation.

Figure – 7: *Resistivity Values as a Function of Boron Concentrations in CdO Films*



CONCLUSION

We have successfully fabricated boron cadmium oxide transparent conducting films on glass substrates by sol-gel spin coating method. The structural, optical and electrical properties were investigated as a function of boron doping. All nano crystalline CdO:B thin films exhibit cubic crystal structure and the grain size was decreased with increasing boron doping. From SEM micrograph the entire boron doped films exhibit well packed spherical shaped grains. The EDX spectrum reveals that the presents Cd, O and B elements in the prepared films. The transmittance is increased with increasing boron concentration and the maximum recorded transmittance is 87% for 5 wt % boron concentration. The optical band gap of undoped and boron doped cadmium oxide films were estimated to be in the range of 2.23 to 2.59eV. The 2.5wt% boron doped CdO thin films exhibited the lowest average electrical resistivity in order of $1.76\times10^{-3}\ \Omega$ cm. These low electrical resistivity and improved band gap thin films can be a good candidate for optoelectronic devices.

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